THE DISPROPORTIONATION OF CERTAIN p-ALKYLTRIPHENYLMETHYLS

BY

WILLIAM HOLLEY RIEGER

A.B., University of Louisville, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF
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INTRODUCTION

Hexa-*p*-tolylethane has been found to be dissociated in solution to the extent of 16 per cent.[1] When the solution is allowed to stand this value decreases and after twenty-four hours is zero. This loss of free radical activity with time has been encountered with certain other *p*-alkyltriphenylmethyls. The present investigation was undertaken to find the explanation for this behavior.

EXPERIMENTAL AND DISCUSSION

A solution of hexa-*p*-tolylethane was prepared by treating a carefully purified sample of tri-*p*-tolylchloromethane with molecular silver. The light orange solution absorbed oxygen to give the expected peroxide and contained tri-*p*-tolylmethyl in an amount which represented a 16 per cent dissociation of the ethane. After twenty-four hours the color had faded to a pale yellow and the solution no longer absorbed oxygen. Removal of the solvent left a glassy residue which reacted with bromine to give tri-*p*-tolylbromomethane and which, when distilled at a pressure of 10^{-4} mm. and a temperature of 85°, gave pure tri-*p*-tolylmethane as a distillate and left a polymeric residue.

Tri-*p*-tolylchloromethane was allowed to react with pyridine according to the method of Schlenk and Meyer.[2] The products were pyridine hydrochloride and a polymer apparently identical with that obtained from the decomposition of tri-*p*-tolylmethyl. The polymers were compared by means of their ultra-violet absorption spectra; solutions of tri-*p*-tolylmethyl and 1,1-di-*p*-tolylquinonedimethane from the pyridine reaction were compared by means of their visible absorption spectra. Attempts to isolate compounds of the quinonedimethane type were unsuccessful.

The mechanism proposed to account for the decomposition of tri-*p*-tolylmethyl involves the reaction of one free radical with another, resulting in the loss of hydrogen from the para methyl group and the formation of tri-*p*-tolylmethane. The other product, a di-free radical, undergoes an electron shift with the formation of 1,1-di-*p*-tolylquinonedimethane which then polymerizes.

Studies on other *p*-alkyltriphenylmethyls showed that a similar mechanism could be applied to account for their behavior. All radicals substituted in the para position by alkyl groups containing a hydrogen atom on the carbon adjacent to the ring were found

to decompose on standing, while those with alkyl groups containing a completely substituted carbon atom next to the ring were stable.

SUMMARY

Tri-*p*-tolylmethyl has been found to undergo disproportionation to give tri-*p*-tolylmethane and a polymeric substance. The reaction of tri-*p*-tolylchloromethane with pyridine has led to the formation of a polymer apparently identical with the polymer from the disproportionation of the radical. A mechanism has been proposed to explain the disproportionation of tri-*p*-tolylmethyl and of other *p*-alkyltriphenylmethyls.

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[2] Schlenk and Meyer, Ber. **52**, 9 (1919).

VITA

The author was born in Louisville, Kentucky, on February 1, 1915. He attended the public and parochial schools of that city and Louisville Male High School. He was granted the degree of Bachelor of Arts from the University of Louisville in June, 1937, and in September of the same year he entered the Graduate School of the University of Illinois. From February, 1938, until June, 1940, he held a teaching assistantship in chemistry. For the year 1940-1941 he held an appointment as research assistant for the National Defense Research Committee.

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